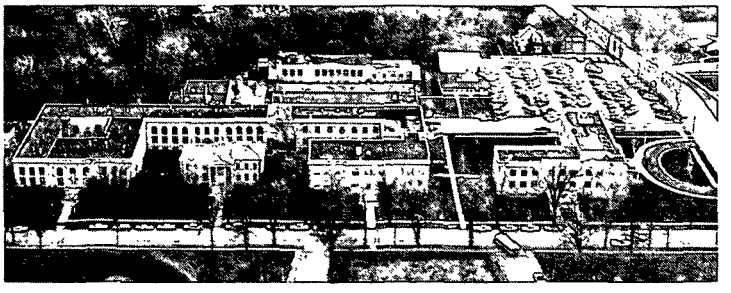

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SULFUR RELEASE AND RETENTION DURING COMBUSTION OF KRAFT BLACK LIQUOR

JAMES G. CANTRELL AND DAVID T. CLAY

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ABSTRACT

Single droplets of black liquor were burned under a variety of conditions to study sulfur release and retention. The significant influencing variables, in decreasing order, were droplet size, solids content, and the oxygen content of the surrounding gas. In general, the sulfur release and the reaction rate decreased with larger droplets, higher solids, and higher oxygen levels.

INTRODUCTION

Black liquor is a substance produced from the kraft pulping process. It contains the dissolved lignin, various organic by-products and the spent cooking chemicals, including sodium sulfide, sodium carbonate, sodium sulfate, sodium hydroxide and various sodium organic compounds. It is concentrated to 65-75% solids before being sprayed into the recovery boiler. In the recovery furnace, the organics are combusted, with the resulting energy release used for steam generation. More importantly, the cooking chemicals, sodium sulfide and sodium carbonate, are recovered as smelt from the furnace.

The kraft process is unique because it uses sodium sulfide, which produces greater fiber strength and results in a higher yield. Although the use of sodium sulfide has great advantages, the introduction of sulfur into the pulp mill causes potentially odorous emissions from the recovery boiler. Strict EPA guidelines on total reduced sulfur gas release and the high cost of makeup cooking chemicals makes the recovery of sulfur an absolute necessity. Other problems associated with high levels of sulfur gas emission are corrosion of boiler tubes and harder to remove tube deposits. Although most of the sulfur can be recovered as sodium sulfate in electrostatic precipitators or in sulfur dioxide scrubbers, the preferred and more economical way of maximizing the recovery of sulfur is to control it at the source, which is the burning particle.

Most of the studies on sulfur gas release have been mill studies on recovery boilers (1,2). These studies have indicated that spray coarseness and solids content have a significant effect on sulfur gas release. Coarser sprays and higher solids content reduce sulfur gas release. Only recently has the combustion of black liquor been studied on single particles (3-5). From these

studies, various stages of combustion were identified as follows: (I) drying, (II) pyrolysis and combustion of volatiles, (III) char burning and (IV) inorganic reactions.

The present study uses the single particle burning technique to observe the effect of the important process variables including particle size, solids content, added sulfur (either as sodium sulfate or emulsified), and oxygen content of the gas stream. The purpose of this work was to gain a better understanding of the kinetic release of sulfur gas in the recovery boiler in order to minimize sulfur losses from the recovery boiler furnace cavity.

APPROACH

The radiant single particle reactor used for this study is shown in figure 1. The description and major details of the apparatus, procedure, black liquor synthesis and data analysis are given in the appendix. A black liquor particle was placed within the reactor. As the burning proceeded, air, nitrogen or a mixture of the two, entered the gas inlet and carried the combustion gases through the outlet. The major mode of heat transfer to the particle was by radiation. The furnace temperature was maintained at about 1090 deg C for all experiments. Combustion gases leaving the gas outlet proceeded to a sulfur dioxide analyzer, which measured sulfur dioxide concentration as a function of time. A computer in conjunction with an analog/digital interface was used for data acquisition.

The major process variables studied were particle size, solids content, added sulfur and gas stream oxygen content. Particle size and solids content were varied at four different levels with each combination being studied. The

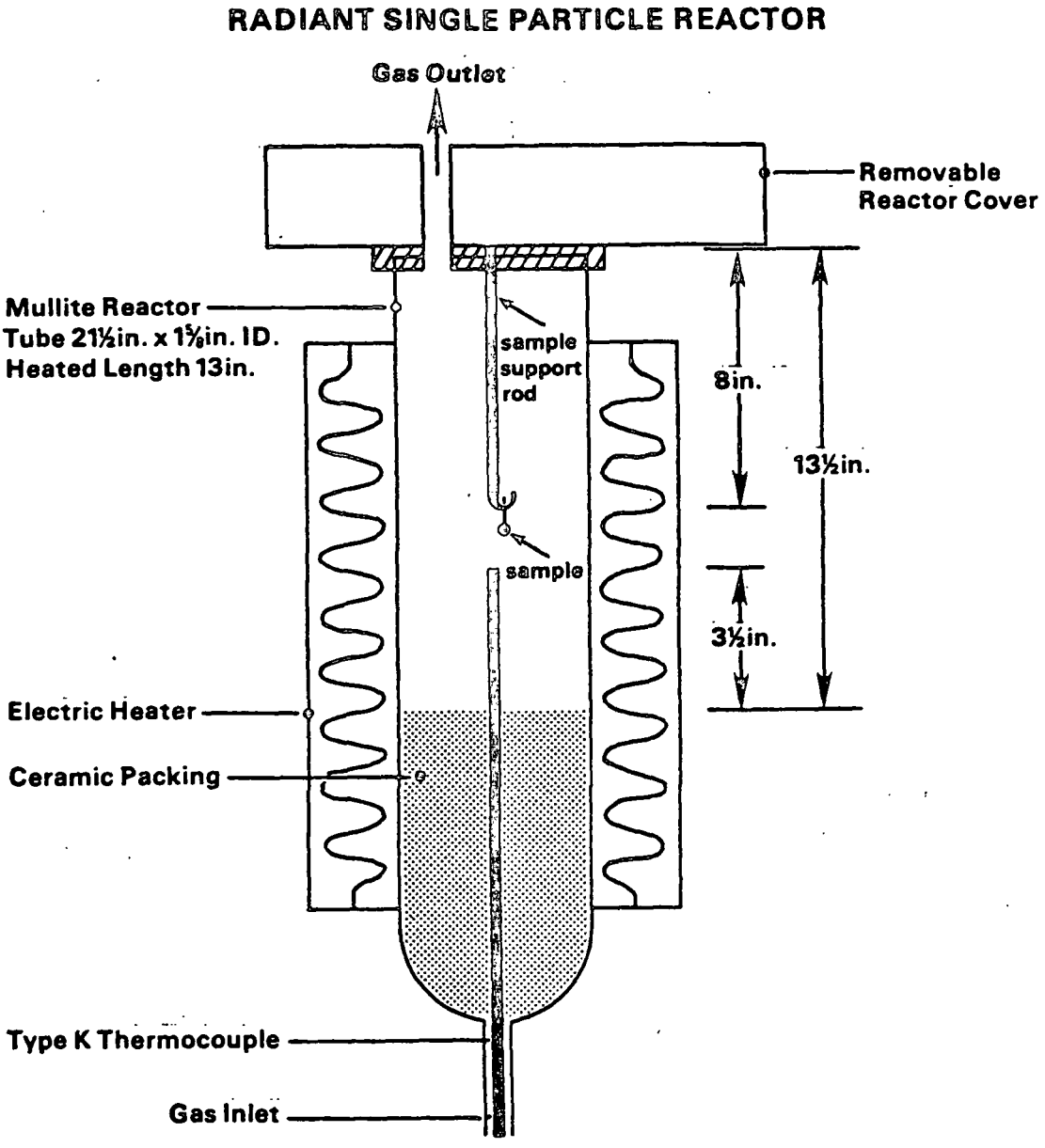

Figure 1. Radiant Single Particle Reactor

particle size and solids content that maximized sulfur release were used in the added sulfur and gas stream oxygen content experiments. All conditions used in the experimental runs are given in table 1.

RESULTS

Particle size had the greatest effect on sulfur gas release. From figure 2, one can see that as particle size is increased the total sulfur released decreases in an exponential fashion approaching some constant value. Also, as particle size is increased, the rate constant decreases as seen in figure 3.

Solids content had only a moderate effect on sulfur release. As solids content increases, the total sulfur released decreases. This effect becomes much less noticeable as particle size increases. For large particles, it appears that the particle size effect is controlling as can be seen in figure 4. The rate constant decreases as solids content increases until it reaches a minimum at about 85% solids. Then the rate constant begins to increase rather sharply as dry solids content is approached as shown in figure 5.

Although the oxygen content of the gas stream did not affect the normalized rate of sulfur release, it had a significant effect on the total sulfur released. At about 13% oxygen the percent total sulfur released reaches a maximum of about 75% for this particular system. This can be seen in figure 6.

Table 1. Particle Burn Conditions

Experiment	Diameter (mm)	% Solids	% Sulfur (E or S)	% Oxygen
Size + % Solids	1.0	63.3	3.34	21.0
"	2.0	"	"	"
"	3.0	"	"	"
"	4.0	"	"	"
"	1.0	71.9	"	"
"	2.0	"	"	"
"	3.0	"	"	"
"	4.0	"	"	"
"	1.0	83.3	"	"
"	2.0	"	"	"
"	3.0	"	"	"
"	4.0	"	"	"
"	1.0	98.9	"	"
"	2.0	"	"	"
"	3.0	"	"	"
"	4.0	"	"	"
Added Sulfur	2.0	63.3	"	"
"	"	64.4	4.29 E	"
"	"	66.1	5.26 E	"
"	"	63.9	5.59 S	"
"	"	68.0	6.17 E	"
% Oxygen	"	63.3	3.34	21.0
"	"	"	"	15.4
"	"	"	"	10.5
"	"	"	"	5.6
"	"	"	"	0.0

E = added as emulsified sulfur

S = added as sodium sulfate

Furnace temperature = 1090 deg C

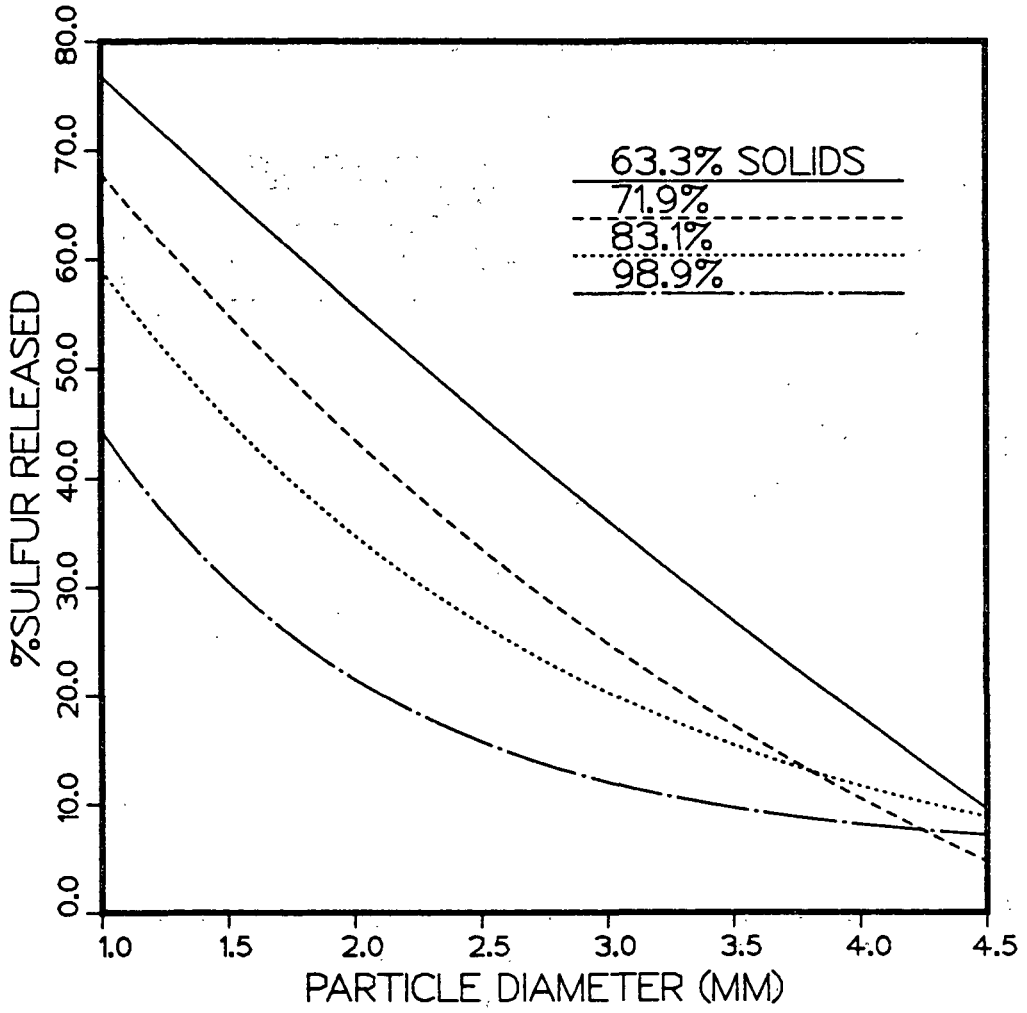

Figure 2. % Initial Sulfur Released vs. Particle Diameter

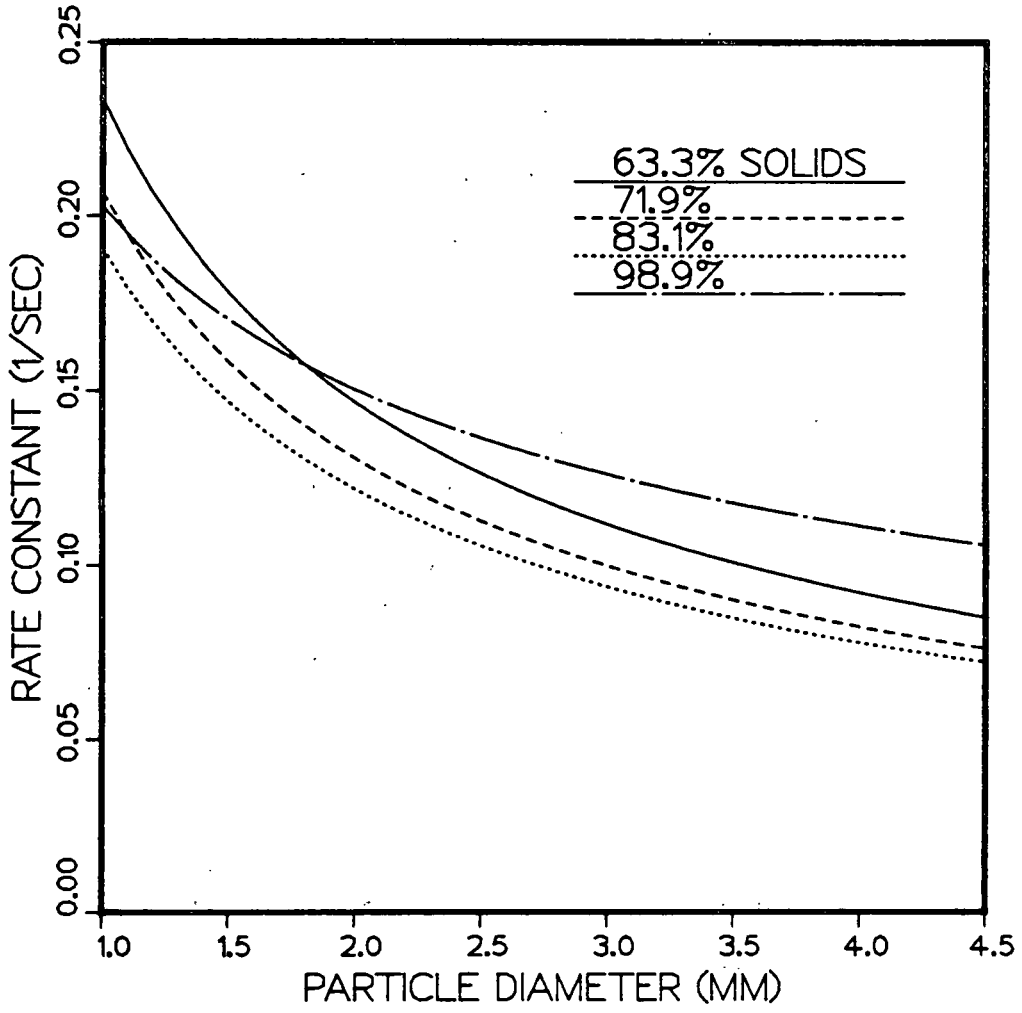

Figure 3. Rate Constant vs. Particle Diameter

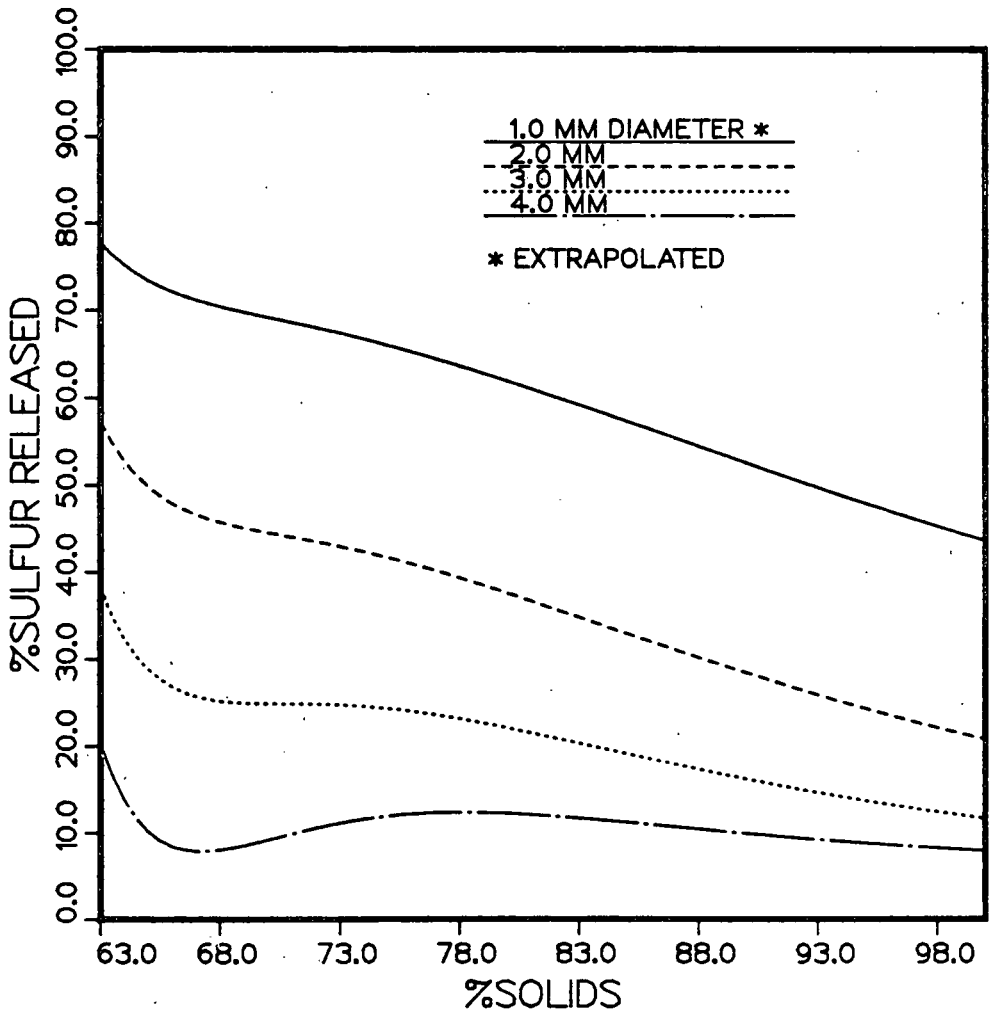

Figure 4. % Initial Sulfur Released vs. Solids Content

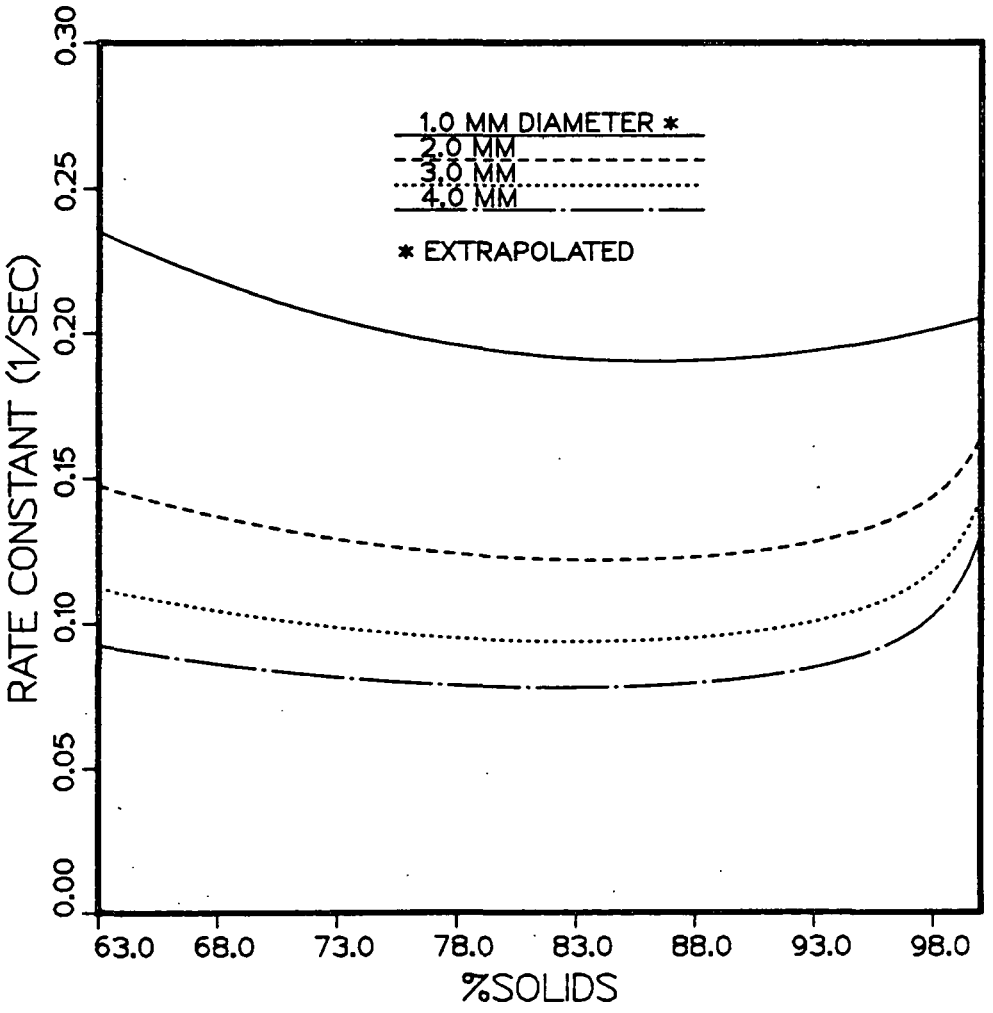

Figure 5. Rate Constant vs. Solids Content

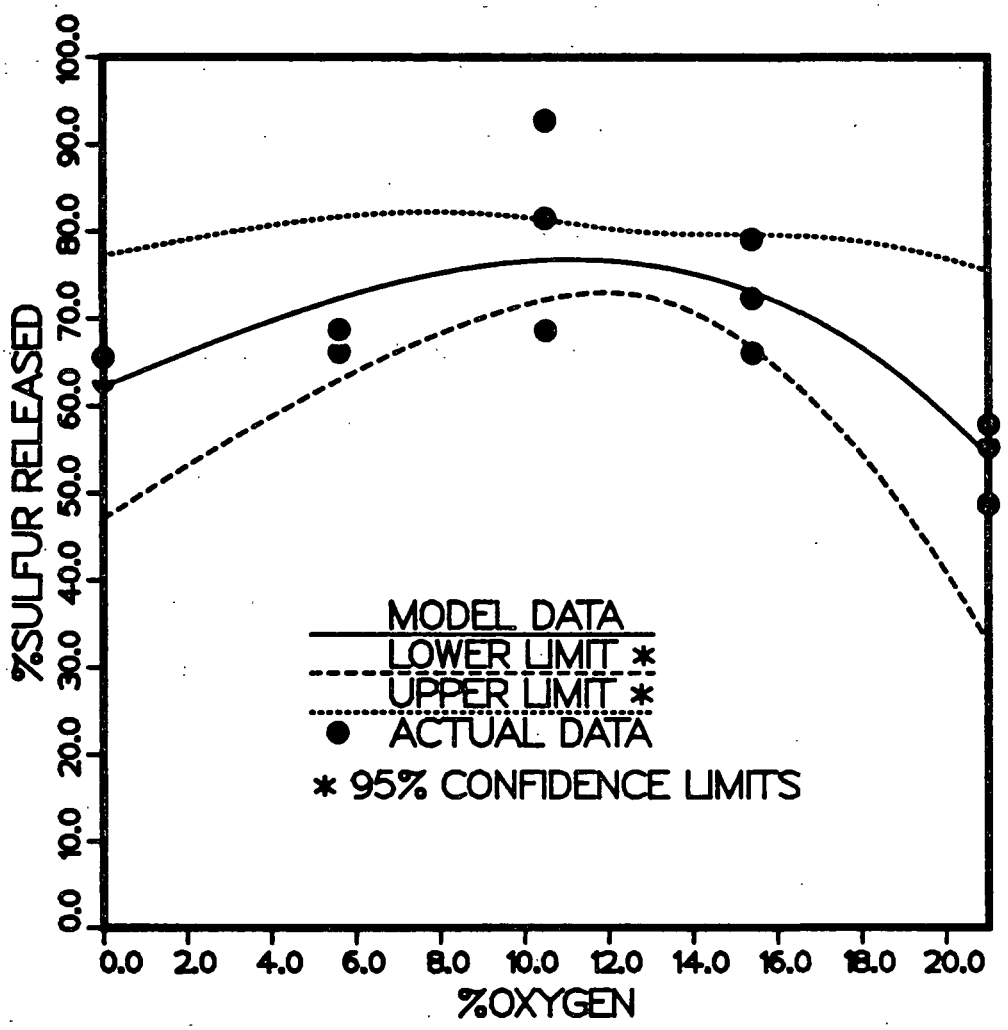

Figure 6. % Initial Sulfur Released vs. Gas Stream Oxygen Content

DISCUSSION

Four different phases of combustion occur during the combustion of black liquor particles, which are (I) drying, (II) pyrolysis and combustion of volatiles, (III) char burning and, (IV) the inorganic reactions (3). Most of the sulfur gas is released during the pyrolysis stage, which occurs between 250-750 deg C (6). These gases consist mostly of hydrogen sulfide, which is further combusted to sulfur dioxide as it leaves the particle surface. Sodium carbonate is produced during the char burning stage as the sodium-organic compounds combust.

From the present data, one can see that as particle size increases, the percent total sulfur released decreases. For the larger particles there is more of a temperature gradient from the outer to inner portion of the particle during the initial stages of combustion. Figure 7 shows temperature profiles for various particle sizes after two seconds of exposure for an 80% solids black liquor. The larger particles have a vastly greater temperature gradient, which allows for the various combustion stages to occur simultaneously at different radial positions throughout the particle.

The general scenario for larger particles leading to reduced percent sulfur released can be described based on a sodium carbonate capture mechanism. The large temperature gradient within the particle causes the combustion processes to proceed faster in the outer particle. After ignition takes place, a smelt shell abundant in sodium carbonate rapidly forms in the outer particle. At the same time, pyrolysis is occurring in the inner particle because of lower temperatures (500 deg C). Pyrolysis produces gases including various reduced sulfur compounds, predominantly hydrogen sulfide, which drives the swelling

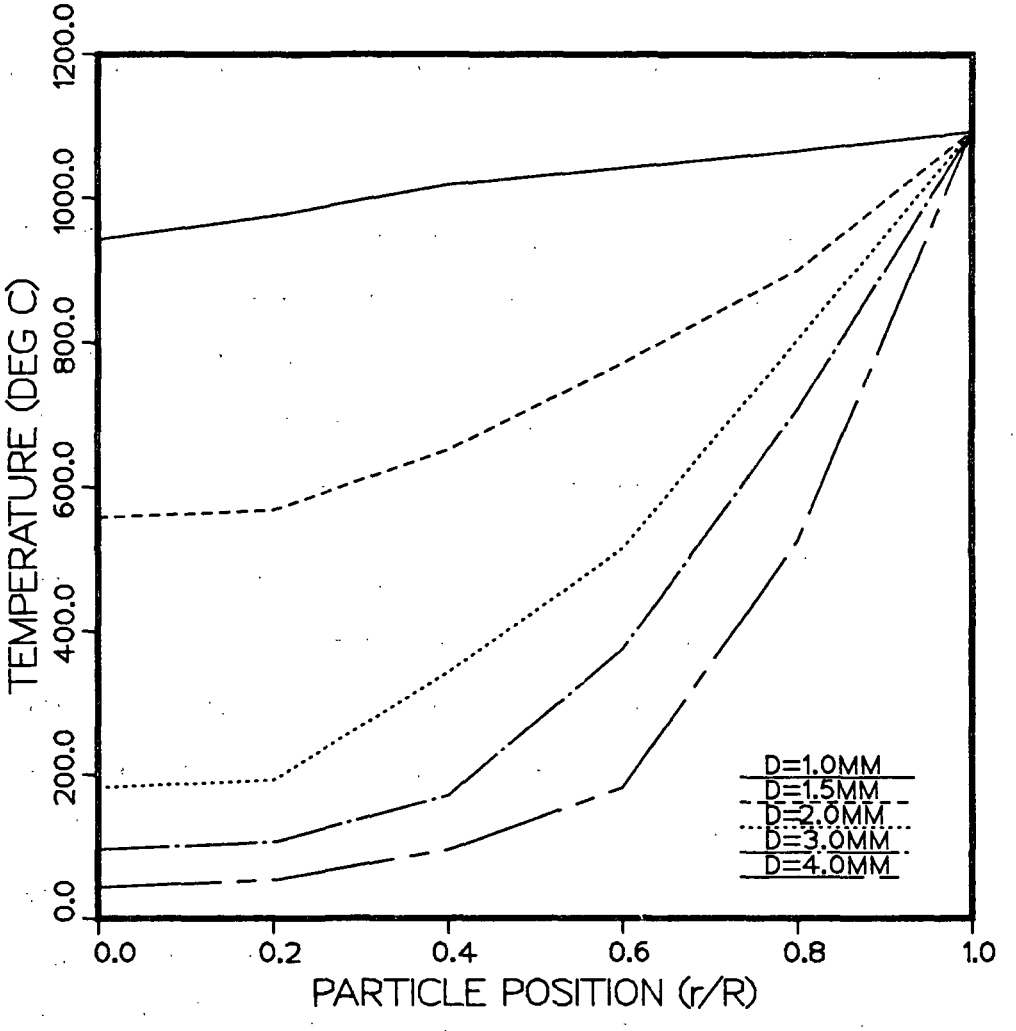

Figure 7. Conductive Temperature Profiles

*Source: Welty, Wicks and Wilson, Fundamentals of Momemtum, Heat and Mass Transfer, Wiley, New York, 2nd ed., 724-725 (1976).
Thermal property data for black liquor from reference (7).

process. As these gases transfer through the outer particle, the sulfur gas is captured by sodium carbonate in the smelt as follows (8):

$$Na_2CO_3 + H_2S = Na_2S + H_2O + CO_2 \quad (1)$$

$$Na_2CO_3 + H_2S + 2O_2 = Na_2SO_4 + CO_2 + H_2O \quad (2)$$

This action causes an overall decrease in the percent total sulfur released as particle size increases.

Smaller particles have much less of a temperature gradient, so the combustion stages occur discretely and uniformly throughout the particle. Any sulfur gas released during the pyrolysis stage is not captured because no smelt exists yet in the outer layer of the particle. This gas is further combusted to sulfur dioxide at the particle surface before leaving the furnace.

As can be seen from figure 4, an increase in solids causes a decrease in sulfur release, but the effect is not as great as the particle size effect. In addition, as particle size increases the solids content has less of an effect. Thermal conductivity and heat capacity decrease while density increases, causing an overall decrease in the thermal diffusivity as solids content increases. This has the net effect of decreasing the release of sulfur and the normalized release rate. Particles of higher solids content are larger than particles of lower solids content for a given particle size after the moisture has been removed. This also decreases the sulfur gas release and normalized release rate for the higher solids content particles.

Added sulfur had no effect on either the total sulfur release or the rate. Sulfur added as sodium sulfate was expected to have no effect, since sulfate is

already in a high oxidation state and is unreactive. Sulfur added as emulsified sulfur apparently reacted with sodium carbonate in the smelt phase to form sodium sulfide and sulfate.

Although oxygen had no effect on the normalized sulfur release rate, there was an observed maximum at around 13% oxygen for the percent total sulfur released. The value of 64% total sulfur released as sulfur dioxide for 0% oxygen is questionable, since it does not take much oxygen to completely combust the TRS compounds to sulfur dioxide. Therefore, it is possible that there may have been air leakage into the system during the experimental runs. At any rate, the observed maximum is probably due to two controlling factors. First, as gas stream oxygen content is initially decreased the combustion temperature and resulting temperature gradient are decreased, allowing more sulfur gas to escape during pyrolysis. Second, as oxygen content is decreased further, there is insufficient oxygen to completely combust all TRS compounds to sulfur dioxide before leaving the furnace. The net result is an observed maximum sulfur dioxide release at 13% oxygen for this system.

CONCLUSIONS

Of all the process variables studied, particle size had the greatest effect on sulfur gas release. As particle size increases, sulfur release decreases. Solids content and gas stream oxygen content had moderate effects. An increase in solids content caused a decrease in sulfur release. This effect becomes less prevalent as particle size increases. Sulfur dioxide release reaches a maximum at around 13% gas stream oxygen content. Added sulfur had no effect on the release of sulfur gas during black liquor burning at 1090 deg C in air.

The temperature profile generated in larger particles enable them to retain more sulfur by the sodium carbonate capture mechanism. Higher solids changes the physical and thermal properties of the black liquor, resulting in sulfur retention similar to large particles, but to a lesser extent. Decreased oxygen content in the gas stream decreases the temperature gradient generated, allowing more sulfur to be released. Sulfur added as emulsified sulfur is apparently captured by sodium carbonate in the smelt phase, resulting in no effect on sulfur release for air at 1090 deg C.

ACKNOWLEDGMENTS

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APPENDIX

APPARATUS

The radiant single particle reactor is shown in figure 1. A mullite reactor surrounded by an electric heater was used to heat the particle. A flow-rate of 240 cc/min was used to minimize convective heat transfer. Ceramic packing was used to maintain a uniform flow of gas to the particle and to aid in heating the incoming gas. A thermocouple coming up through the gas inlet to the locality of the particle was used to measure the furnace temperature, which was kept constant at 1090 deg C. The particle was formed on a wire hook, which rested on the sample support rod during the burn.

The analytical equipment used consisted of a Teledyne series 600 UV photometric sulfur dioxide analyzer. The analyzer continuously measured the concentration of sulfur dioxide in the flue gas stream by measuring the amount of ultraviolet radiation that was absorbed by the gas at a specific frequency characteristic of only sulfur dioxide. The analog signal from the sulfur dioxide analyzer was converted to a digital signal and stored on a floppy disk by a data acquisition system.

All of the experimental runs were carried out in the following manner: (1) forming a black liquor particle of specific size on the end of an inch-long Nichrome wire hook, (2) attaching the sample at the bottom of the sample support rod, (3) activating the data acquisition system to receive data, (4) beginning the burning process by placing the reactor cover in place, (5) removing the cover after about two minutes when the run was over, (6) purging the gas line from the reactor to the analyzer with nitrogen in preparation for the next run,

(7) periodic calibration of the sulfur dioxide analyzer. The time at which the sulfur dioxide concentration began to rise was defined as time zero.

BLACK LIQUOR SYNTHESIS

The black liquor samples were made from a weak black liquor which was obtained from a standard kraft cook of loblolly pine wood chips in a laboratory digester. The cooking conditions are given in table 2.

Table 2. Laboratory Black Liquor Cooking Conditions

Dry Wood = 3600 g

Sodium Sulfide = 345.1 g

Sodium Hydroxide = 637.1 g

Water = 10,947.7 g

Moisture Content = 46.2%

Effective Alkali = 16%

Sulfidity = 25%

H-factor = 1876

Liquor/Wood = 4

Black Liquor Yield = 8 liters

The black liquor was then placed in a rotary evaporator under a vacuum of 90 kPa, in a water bath at approximately 60-70 deg C. When the sample reached 25% solids, the soap residue was removed from the sample by filtering it through a sponge and then the sample was concentrated to about 50% solids. At 50% solids, the sample was placed in an oven at approximately 140 deg C in a nitrogen atmosphere under a vacuum of about 75 kPa. Fifteen gram portions were taken as the black liquor solids reached about 65, 75, 85, and 95% solids. The sulfur

was always added to the 50% solids liquor for the added sulfur samples before continuing the evaporation process.

METHOD OF ANALYSIS

A sample data curve is shown in figure 8 along with the fitted curve. Assuming first order overall release of sulfur along with first order system dynamics the following equation was fit to the data to obtain k, the rate constant:

$$(dS/dt)_{rec} = (e^{-kt} - e^{-t/\tau})K\Delta S/(1-k\tau) \qquad (3)$$

Where dS/dt = % initial sulfur/second, τ = time constant, t = time and ΔS = % total sulfur released. Correlation coefficients for the above equation averaged around 0.8. Delta S was obtained through direct numerical integration of the data curve. After delta S and k were obtained for all the experimental runs, they were fitted to empirical equations for curve representation.

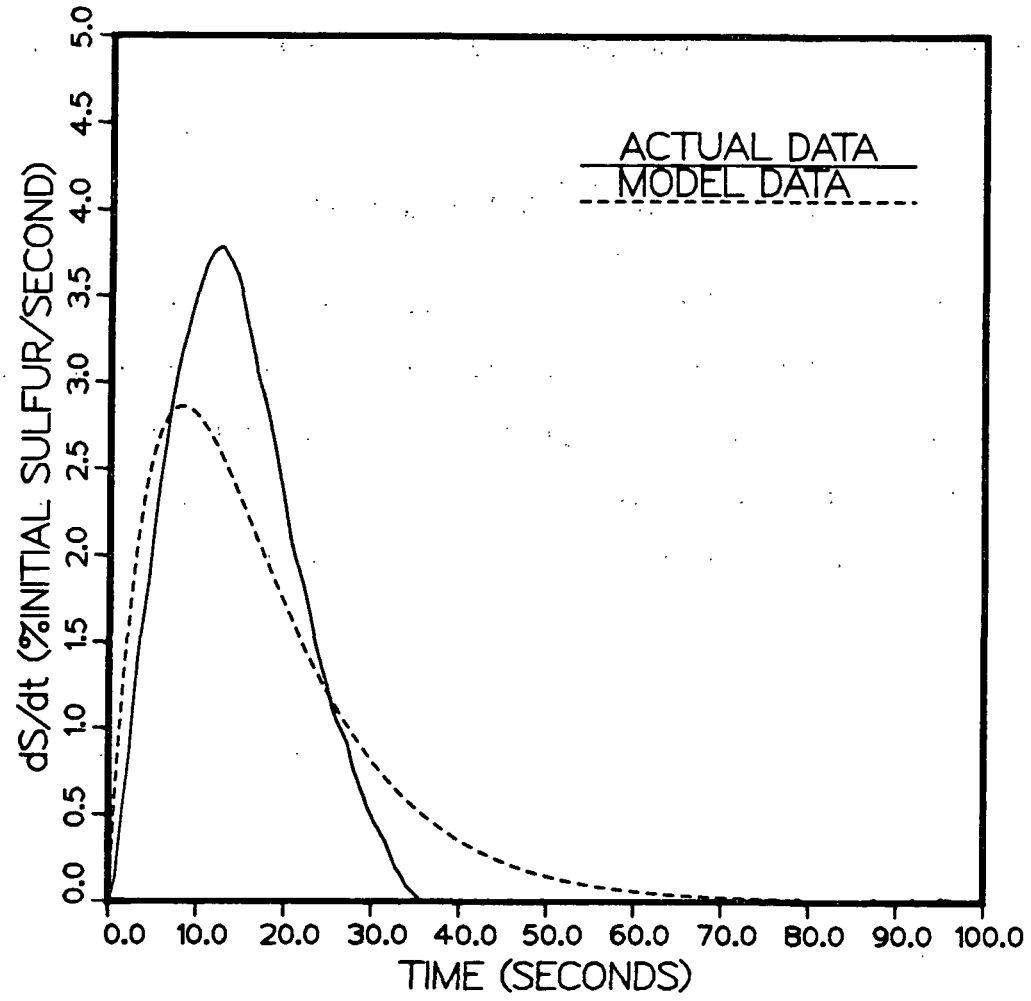

Figure 8. Sample Data Curve (63.3% solids, 2.0 mm dia.)